



NOVEL HETEROAROMATIC TRINUCLEAR BLACK DIRECT DYES

The invention relates to novel heteroaromatic trinuclear direct dyes, to dye compositions containing
5 these dyes and to the process for dyeing keratin fibres using them. In particular, the invention relates to heteroaromatic trinuclear direct dyes comprising a pyridine nucleus.

It is known practice to dye keratin fibres,
10 and in particular human hair, with dye compositions containing direct dyes. The standard dyes that are used are in particular dyes of the nitrobenzene, anthraquinone, nitropyridine, azo, cationic azo, xanthene, acridine, azine, and triarylmethane
15 nitrobenzene type or natural dyes.

These dyes, which are coloured and colouring molecules that show affinity for fibres, are applied to keratin fibres for the time required to obtain the desired coloration, and then rinsed out.

20 The colorations resulting therefrom are particularly chromatic colorations, but are, however, temporary or semi-permanent since the nature of the interactions that link the direct dyes to the keratin fibre, and their desorption from the surface and/or
25 from the core of the fibre are responsible for their weak dyeing power and their poor wash-fastness or resistance to perspiration. These direct dyes are also

generally light-sensitive due to the poor resistance of the chromophore to photochemical attack, and lead to fading of the coloration of the hair over time.

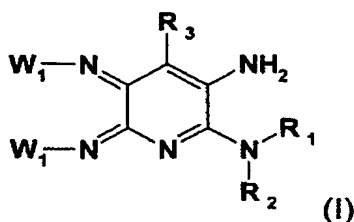
Patent application EP 1 166 754 describes a dye composition comprising cationic phenazinium azo direct dyes. Due to the presence of the azo function, these compounds are unstable when placed in contact with a reducing agent such as erythorbic acid, metabisulphite or sulphite, this instability being reflected in destruction of the chromophoric system.

The aim of the present invention is to provide novel direct dyes that do not have the drawbacks of the prior art, in particular direct dyes that allow dark, black to grey, shades to be obtained, which are light-fast, and resistant to bad weather, washing and perspiration, and are also stable in a standard dyeing medium.

In particular, the aim of the present invention is to provide black direct dyes allowing hair to be dyed in shades ranging from grey to black, without the need to lighten the hair beforehand, and also black direct dyes which, even when fading, do not change shade, for example by changing colour after the action of washing, light or sweat towards shades with blue, violet, red, green, etc. glints. Finally, these black direct dyes should make it possible to maintain,

after several applications, the shade obtained during the first application.

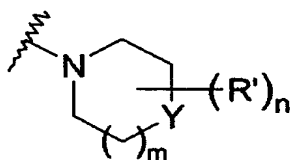
These aims are achieved with the present invention, one subject of which is a dye composition comprising, in a suitable medium, a compound of formula (I) below or an addition salt thereof:



in which

- 10 • R_3 represents:
- a hydrogen atom,
 - a linear or branched C_1 - C_{10} hydrocarbon-based chain, which can form one or more 4- to 8-membered carbon-based rings, and which may be saturated or unsaturated, one or more carbon atoms of the carbon-based chain of which may be replaced with an oxygen, nitrogen or sulphur atom or with an SO_2 group; R_3 not comprising a peroxide bond or diazo or nitroso radicals,
 - $NR'_1R'_2$, R'_1 and R'_2 being as defined for R_1 and R_2 ,
- 15
- 20 • R_1 and R_2 represent, independently of each other:
- a hydrogen atom,

- 5 - a linear or branched C₁-C₁₀ hydrocarbon-based chain, which can form one or more 4- to 8-membered carbon-based rings, and which may be saturated or unsaturated, one or more carbon atoms of the carbon-based chain of which may be replaced with an oxygen, nitrogen or sulphur atom or with an SO₂ group; R₁ and R₂ not comprising a peroxide bond or diazo or nitroso radicals, and R₁ and R₂ not being directly linked to the nitrogen atom via an oxygen, sulphur or nitrogen atom or SO₂,
- 10 - an onium radical Z, or
- 15 • R₁ and R₂ form, together with the nitrogen atom to which they are attached, a ring of formula (II):



formula (II)

in which

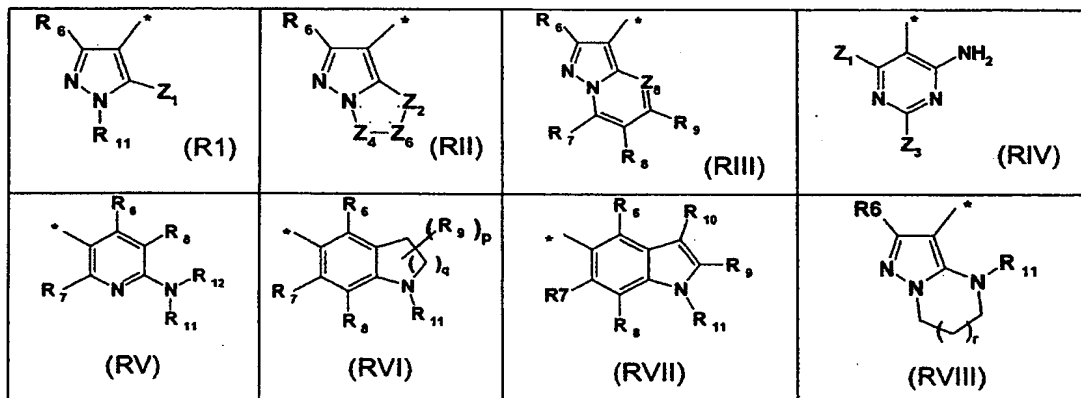
- 20 • R' represents:
- a hydrogen atom;
 - a halogen atom such as fluorine, chlorine or bromine;
 - a C₁-C₄ alkyl radical optionally substituted
- 25 with one or more radicals chosen from

hydroxyl, carboxyl, C₁-C₄ alkoxy carbonyl,
(C₁-C₄) alkylamido ((C₁-C₄) alkylCONH-),
(C₁-C₄) alkylcarbamoyl ((C₁-C₄) alkylNHCO-),
(C₁-C₄) alkylsulphonyl ((C₁-C₄) alkylSO₂-), C₁-C₄
5 alkoxy, (C₁-C₄) alkylsulphonamido
((C₁-C₄) alkylSO₂NH-), (C₁-C₄) alkylsulphamoyl
((C₁-C₄) alkylNH₂SO₂-) and onium Z radicals;
- NR'₃R'₄;
- a carboxyl radical;
10 - a C₁-C₄ alkoxy carbonyl radical;
- a (C₁-C₄) alkylamido radical
((C₁-C₄) alkylCONH-);
- a (C₁-C₄) alkylsulphonyl radical (alkylSO₂-);
- an alkylsulphonamido radical
15 ((C₁-C₄) alkylSO₂NH-);
- a hydroxyl radical;
- a C₁-C₄ alkoxy radical;
- a C₂-C₄ hydroxyalkoxy radical;
- a (C₁-C₄) alkylcarbamoyl radical
20 ((C₁-C₄) alkylNHCO-);
- (C₁-C₄) alkylsulphamoyl ((C₁-C₄) alkyl-NH-
SO₂-);
- a C₁-C₄ thioether radical;
- a sulphonic radical (SO₃H), which may be in
25 salt form;
- an onium radical Z,

R'₃ and R'₄, which may be identical or different,
represent a hydrogen atom; a C₁-C₄ alkyl radical
optionally substituted with one or more radicals chosen
from hydroxyl, C₁-C₄ alkoxy, amino, mono- or
5 dialkylamino, (C₁-C₄)alkylCO-, (C₁-C₄)alkylNHCO- and
(C₁-C₄)alkylSO₂- radicals,
- n is an integer between 1 and 8,
- m is an integer between 0 and 3, preferably from 0 to
2,
10 - Y represents an oxygen atom, a radical CR', a radical
NR'₅ or a radical NR'₆R'₇ with
R'₅ which represents a hydrogen atom; a
linear or branched C₁-C₁₀ hydrocarbon-based
chain, which may be saturated or unsaturated,
15 one or more of the carbon atoms of the
carbon-based chain of which may be replaced
with an oxygen, nitrogen or sulphur atom or
with an SO₂ group; R'₅ not comprising a
peroxide bond or diazo or nitroso radicals,
20 and R'₅ not being directly linked to the
nitrogen atom via an oxygen, sulphur or
nitrogen atom,
R'₆ and R'₇ which represent, independently, a
linear or branched C₁-C₁₀ hydrocarbon-based
25 chain, which may be saturated or unsaturated,
one or more carbon atoms of the carbon-based
chain of which may be replaced with an

oxygen, nitrogen or sulphur atom or with an
SO₂ group; R'₆ and R'₇ not comprising a
peroxide bond or diazo or nitroso radicals,
and R'₆ and R'₇ not being directly linked to
the nitrogen atom via an oxygen, sulphur or
nitrogen atom,

- W₁ represents an aromatic heterocyclic radical
chosen from the following radicals



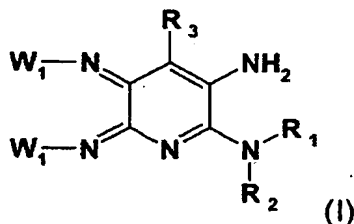
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- Z₁ and Z₃ represent, independently of each other, a
hydroxyl or NR₁₁R₁₂ radical,
- Z₂, Z₄ and Z₆ represent, independently of each
other, a nitrogen atom or a radical CR₁₂ or NR₁₁,
with the proviso that at least one of them
represents a radical CR₁₂ and that there cannot be
more than three contiguous nitrogen atoms,
- Z₈ represents a nitrogen atom or a radical CR₁₅,
- R₆, R₇, R₈, R₉, R₁₀, R₁₁, R₁₂ and R₁₅ represent,
independently of each other:
- a hydrogen atom,

20

- 5
- 10
- 15
- a linear or branched C₁-C₁₀ hydrocarbon-based chain, which can form one or more 4- to 8-membered carbon-based rings, and which may be saturated or unsaturated, one or more carbon atoms of the carbon-based chain of which may be replaced with an oxygen, nitrogen or sulphur atom or with an SO₂ group; the radicals R₆ to R₁₂ and R₁₅ not comprising a peroxide bond or diazo or nitroso radicals, and the radical R₁₁ not being directly linked to the nitrogen atom via an oxygen, sulphur or nitrogen atom,
 - p may take the values 4 to 8,
 - q may take the values 1 to 3, and
 - r may take the values 0 to 2,
 - * indicates the point of attachment of W₁ in formula (I).

20 dye composition according to the present invention comprises, in a suitable medium, a compound of formula (I) below or an addition salt thereof:



in which

• R_3 represents:

- a hydrogen atom,
- a linear or branched C_1 - C_{10} hydrocarbon-
based chain, which can form one or more 4- to
5 8-membered carbon-based rings, and which may
be saturated or unsaturated, one or more
carbon atoms of the carbon-based chain of
which may be replaced with an oxygen,
nitrogen or sulphur atom or with an SO_2
10 group, and the carbon atoms of which may be,
independently of each other, substituted with
one or more halogen atoms or hydroxyl, amino,
carboxyl, sulphonic or thiol radicals; R_3 not
comprising a peroxide bond or diazo or
15 nitroso radicals,

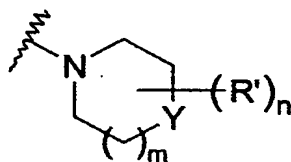
- $NR'_1R'_2$, R'_1 and R'_2 being as defined for R_1
and R_2

• R_1 and R_2 represent, independently of each other:

- a hydrogen atom
20 - a linear or branched C_1 - C_{10} hydrocarbon-
based chain, which can form one or more 4- to
8-membered carbon-based rings, and which may
be saturated or unsaturated, one or more
carbon atoms of the carbon-based chain of
25 which may be replaced with an oxygen,
nitrogen or sulphur atom or with an SO_2
group, and the carbon atoms of which may be,

independently of each other, substituted with
 one or more halogen atoms or hydroxyl, amino,
 carboxyl, sulphonic or thiol radicals; R_1 and
 R_2 not comprising a peroxide bond or diazo or
 5 nitroso radicals, and R_1 and R_2 not being
 linked directly to the nitrogen atom via an
 oxygen, sulphur or nitrogen atom or SO_2 ,
 - an onium radical Z, or

- R_1 and R_2 form, together with the nitrogen atom to
 10 which they are attached, a ring of formula (II):



formula (II)

in which:

- 15 • R' represents:
 - a hydrogen atom;
 - a halogen atom such as fluorine, chlorine
or bromine;
 - a C_1 - C_4 alkyl radical optionally substituted
 20 with one or more radicals chosen from
 hydroxyl, carboxyl, C_1 - C_4 alkoxy carbonyl, (C_1 -
 C_4)alkylamido ((C_1 - C_4)alkylCONH-), (C_1 -
 C_4)alkylcarbamoyl ((C_1 - C_4)alkylNHCO-), (C_1 -
 C_4)alkylsulphonyl ((C_1 - C_4)alkyl SO_2 -), C_1 - C_4
 25 alkoxy, (C_1 - C_4)alkylsulphonamido((C_1 -

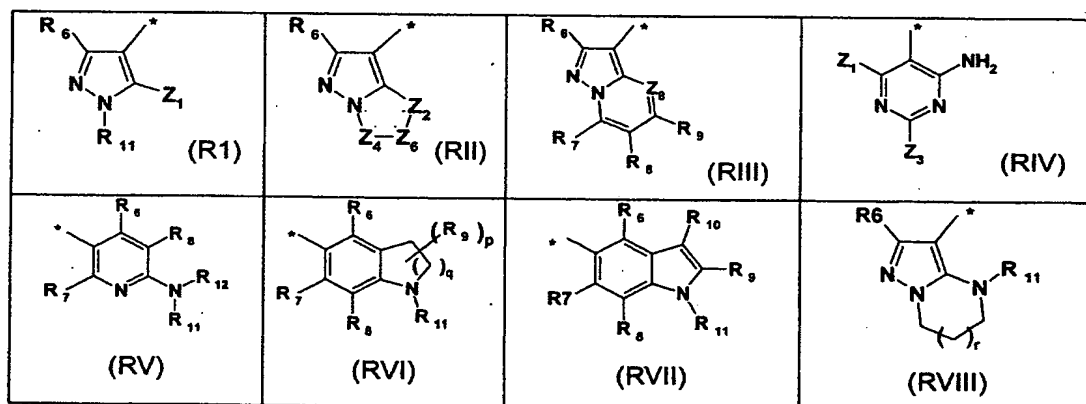
- C₄)alkylSO₂NH-), (C₁-C₄)alkylsulphamoyl ((C₁-C₄)alkylNHSO₂-), and onium Z radicals,
- NR'₃R'₄;
 - a carboxyl radical;
 - 5 - a C₁-C₄ alkoxy carbonyl radical;
 - a (C₁-C₄)alkylamido radical ((C₁-C₄)alkylCONH-);
 - a (C₁-C₄)alkylsulphonyl radical (alkylSO₂-);
 - an alkylsulphonamido radical ((C₁-C₄)alkylSO₂NH-);
 - 10 - a hydroxyl radical;
 - a C₁-C₄ alkoxy radical;
 - a C₂-C₄ hydroxyalkoxy radical;
 - a (C₁-C₄)alkylcarbamoyl radical ((C₁-C₄)alkylNHCO-);
 - 15 - (C₁-C₄)alkylsulphamoyl ((C₁-C₄)alkyl-NH-SO₂-);
 - a C₁-C₄ thioether radical;
 - a sulphonic radical (SO₃H) which may be in salt form;
 - 20 - an onium radical Z;
- R'₃ and R'₄, which may be identical or different, represent a hydrogen atom; a C₁-C₄ alkyl radical optionally substituted with one or more radicals chosen from hydroxyl, C₁-C₄ alkoxy, amino, monoalkylamino, dialkylamino, (C₁-C₄)alkylCO-, (C₁-C₄)alkylNHCO- and (C₁-C₄)alkylSO₂- radicals,
- n is an integer between 1 and 8,

- m is an integer between 0 and 3 and preferably between 0 and 2,
- Y represents an oxygen atom, a radical CR', a radical NR'₅ or a radical NR'₆R'₇, with

5 R'₅ which represents a hydrogen atom; a
linear or branched C₁-C₁₀ hydrocarbon-based
chain, which may be saturated or unsaturated,
one or more carbon atoms of the carbon-based
chain of which may be replaced with an
10 oxygen, nitrogen or sulphur atom or with an
SO₂ group, and the carbon atoms of which may
be, independently of each other, substituted
with one or more halogen atoms or hydroxyl,
amino, carboxyl, sulphonic or thiol radicals;
15 R'₅ not comprising a peroxide bond or diazo
or nitroso radicals, and R'₅ not being linked
directly to the nitrogen atom via an oxygen,
sulphur or nitrogen atom,
R'₆ and R'₇ which independently represent a
20 linear or branched C₁-C₁₀ hydrocarbon-based
chain, which may be saturated or unsaturated,
one or more carbon atoms of the carbon-based
chain of which may be replaced with an
oxygen, nitrogen or sulphur atom or with an
25 SO₂ group, and the carbon atoms of which may
be, independently of each other, substituted
with one or more halogen atoms or hydroxyl,

amino, carboxyl, sulphonic or thiol radicals;
R'₆ and R'₇ not comprising a peroxide bond or
diazo or nitroso radicals, and R'₆ and R'₇ not
being linked directly to the nitrogen atom
5 via an oxygen, sulphur or nitrogen atom,

- W₁ represents an aromatic heterocyclic radical
chosen from the following radicals



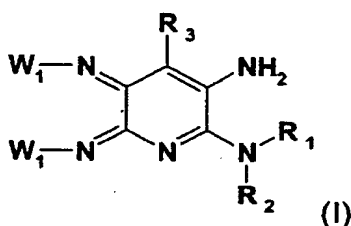
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- Z₁ and Z₃ represent, independently of each other, a hydroxyl radical or a radical NR₁₁R₁₂;
- Z₂, Z₄ and Z₆ represent, independently of each other, a nitrogen atom or a radical CR₁₂ or NR₁₁,
15 with the proviso that at least one of them represents a radical CR₁₂ and that there cannot be more than three contiguous nitrogen atoms,
- Z₈ represents a nitrogen atom or a radical CR₁₅;
- R₆, R₇, R₈, R₉, R₁₀, R₁₁, R₁₂ and R₁₅ represent,
20 independently of each other:

- a hydrogen atom,

- 5 - a linear or branched C₁-C₁₀ hydrocarbon-based chain, which can form one or more 4- to 8-membered carbon-based rings, and which may be saturated or unsaturated, one or more carbon atoms of the carbon-based chain of which may be replaced with an oxygen, nitrogen or sulphur atom or with an SO₂ group, and the carbon atoms of which may be, independently of each other, substituted with one or more 10 halogen atoms or hydroxyl, amino, carboxyl, sulphonic or thiol radicals; the radicals R₆ to R₁₂ and R₁₅ not comprising a peroxide bond or diazo or 15 nitroso radicals and the radical R₁₁ not being linked directly to the nitrogen atom via an oxygen, sulphur or nitrogen atom,
- 20 - p can take the values 4 to 8,
 - q can take the values 1 to 3, and
 - r can take the values 0 to 2,
 - * indicates the point of attachment of W₁ in formula (I).

25 According to another particular embodiment, the dye composition according to the present invention comprises, in a suitable medium, a compound of formula (I) below or an addition salt thereof:



in which

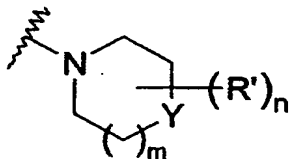
- R₃ represents:

- a hydrogen atom,
- a linear or branched C₁-C₁₀ hydrocarbon-based chain, which can form one or more 4- to 8-membered carbon-based rings, and which may be saturated or unsaturated, one or more carbon atoms of the carbon-based chain of which may be replaced with an oxygen, nitrogen or sulphur atom or with an SO₂ group, and the carbon atoms of which may be, independently of each other, substituted with one or more halogen atoms or hydroxyl, amino, C₁-C₂ (di)alkylamino, C₁-C₂ alkoxy, carboxyl, sulphonic or thiol radicals; R₃ not comprising a peroxide bond or diazo or nitroso radicals,
- NR'₁R'₂, R'₁ and R'₂ being as defined for R₁ and R₂

- R₁ and R₂ represent, independently of each other:

- a hydrogen atom

- 5 - a linear or branched C₁-C₁₀ hydrocarbon-
based chain, which can form one or more 4- to
8-membered carbon-based rings, and which may
be saturated or unsaturated, one or more
carbon atoms of the carbon-based chain of
which may be replaced with an oxygen,
nitrogen or sulphur atom or with an SO₂
group, and the carbon atoms of which may be,
independently of each other, substituted with
10 one or more halogen atoms or hydroxyl, amino,
C₁-C₂ (di)alkylamino, C₁-C₂ alkoxy, carboxyl,
sulphonic or thiol radicals; R₁ and R₂ not
comprising a peroxide bond or diazo or
nitroso radicals, and R₁ and R₂ not being
15 linked directly to the nitrogen atom via an
oxygen, sulphur or nitrogen atom or SO₂,
- an onium radical Z, or
- R₁ and R₂ form, together with the nitrogen atom to
which they are attached, a ring of formula (II):



20

formula (II)

in which:

- R' represents:
 - a hydrogen atom;

- a halogen atom such as fluorine, chlorine or bromine;
- a C₁-C₄ alkyl radical optionally substituted with one or more radicals chosen from
- 5 hydroxyl, carboxyl, C₁-C₄ alkoxy carbonyl, (C₁-C₄)alkylamido ((C₁-C₄)alkylCONH-), (C₁-C₄)alkylcarbamoyl ((C₁-C₄)alkylNHCO-), (C₁-C₄)alkylsulphonyl ((C₁-C₄)alkylSO₂-), C₁-C₄ alkoxy, (C₁-C₄)alkylsulphonamido ((C₁-
- 10 C₄)alkylSO₂NH-), (C₁-C₄)alkylsulphamoyl ((C₁-C₄)alkylNHSO₂-), and onium Z radicals,
- NR'₃R'₄;
- a carboxyl radical;
- a C₁-C₄ alkoxy carbonyl radical;
- 15 - a (C₁-C₄)alkylamido radical ((C₁-C₄)alkylCONH-);
- a (C₁-C₄)alkylsulphonyl radical (alkylSO₂-);
- an alkylsulphonamido radical ((C₁-C₄)alkylSO₂NH-);
- 20 - a hydroxyl radical;
- a C₁-C₄ alkoxy radical;
- a C₂-C₄ hydroxyalkoxy radical;
- a (C₁-C₄)alkylcarbamoyl radical ((C₁-C₄)alkylNHCO-);
- 25 - (C₁-C₄)alkylsulphamoyl ((C₁-C₄)alkyl-NH-SO₂-);
- a C₁-C₄ thioether radical;

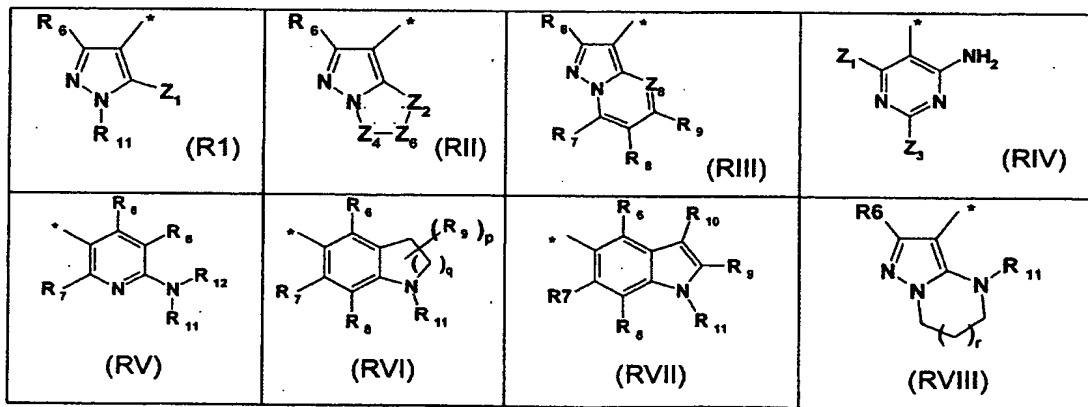
- a sulphonic radical (SO_3H) which may be in salt form;
- an onium radical Z;

R'_3 and R'_4 , which may be identical or different,

- 5 represent a hydrogen atom; a C_1 - C_4 alkyl radical optionally substituted with one or more radicals chosen from hydroxyl, C_1 - C_4 alkoxy, amino, monoalkylamino, dialkylamino, $(\text{C}_1$ - C_4)alkylCO-, $(\text{C}_1$ - C_4)alkylNHCO- and $(\text{C}_1$ - C_4)alkyl SO_2 - radicals,
- 10 - n is an integer between 1 and 8,
- m is an integer between 0 and 3 and preferably between 0 and 2,
- Y represents an oxygen atom, a radical CR' , a radical NR'_5 or a radical $\text{NR}'_6\text{R}'_7$, with
- 15 R'_5 which represents a hydrogen atom; a linear or branched C_1 - C_{10} hydrocarbon-based chain, which may be saturated or unsaturated, one or more carbon atoms of the carbon-based chain of which may be replaced with an
- 20 oxygen, nitrogen or sulphur atom or with an SO_2 group, and the carbon atoms of which may be, independently of each other, substituted with one or more halogen atoms or hydroxyl, amino, carboxyl, sulphonic or thiol radicals;
- 25 R'_5 not comprising a peroxide bond or diazo or nitroso radicals, and R'_5 not being linked

directly to the nitrogen atom via an oxygen,
 sulphur or nitrogen atom,
 R'₆ and R'₇ which independently represent a
 linear or branched C₁-C₁₀ hydrocarbon-based
 chain, which may be saturated or unsaturated,
 one or more carbon atoms of the carbon-based
 chain of which may be replaced with an
 oxygen, nitrogen or sulphur atom or with an
 SO₂ group, and the carbon atoms of which may
 be, independently of each other, substituted
 with one or more halogen atoms or hydroxyl,
 amino, carboxyl, sulphonic or thiol radicals;
 R'₆ and R'₇ not comprising a peroxide bond or
 diazo or nitroso radicals, and R'₆ and R'₇ not
 being linked directly to the nitrogen atom
 via an oxygen, sulphur or nitrogen atom,

- W₁ represents an aromatic heterocyclic radical
 chosen from the following radicals

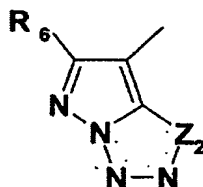


- Z_1 and Z_3 represent, independently of each other, a hydroxyl radical or a radical $NR_{11}R_{12}$;
- Z_2 , Z_4 and Z_6 represent, independently of each other, a nitrogen atom or a radical CR_{12} or NR_{11} ,
5 with the proviso that at least one of them represents a radical CR_{12} and that there cannot be more than three contiguous nitrogen atoms,
- Z_8 represents a nitrogen atom or a radical CR_{15} ;
- R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} , R_{12} and R_{15} represent,
10 independently of each other:
 - a hydrogen atom,
 - a linear or branched C_1 - C_{10} hydrocarbon-based chain, which can form one or more 4- to 8-membered carbon-based rings, and
15 which may be saturated or unsaturated, one or more carbon atoms of the carbon-based chain of which may be replaced with an oxygen, nitrogen or sulphur atom or with an SO_2 group, and the carbon
20 atoms of which may be, independently of each other, substituted with one or more halogen atoms or hydroxyl, amino, carboxyl, sulphonic or thiol radicals;
the radicals R_6 to R_{12} and R_{15} not
25 comprising a peroxide bond or diazo or nitroso radicals and the radical R_{11} not being linked directly to the nitrogen

atom via an oxygen, sulphur or nitrogen
atom,

- p can take the values 4 to 8,
- q can take the values 1 to 3, and
- r can take the values 0 to 2,
- * indicates the point of attachment of W_1
in formula (I).

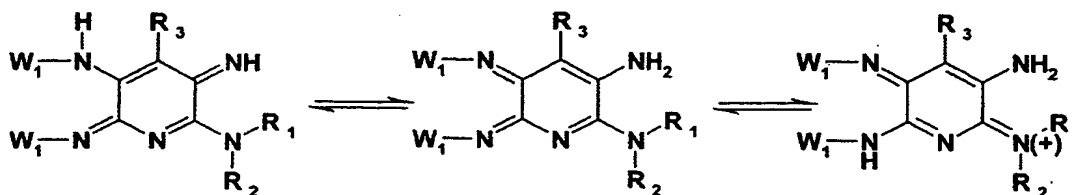
When, in the definition of Z_2 , Z_4 and Z_6 which
represent, independently of each other, a nitrogen atom
or a radical CR_{12} or NR_{11} , it is specified that there
cannot be more than 3 contiguous nitrogen atoms, this
means that it is not possible, for example, to obtain
the following structure



A subject of the present invention is also a
dye composition containing, in a suitable medium, at
least one direct dye of the present invention. The
composition of the present invention is particularly
useful for dyeing keratin fibres, in particular human
keratin fibres.

In the context of the present invention, the
compounds of formula (I) are not only those described

by formula (I), but any other tautomeric form, for instance the following tautomeric form:



5

In the examples that are given in the description hereinbelow, only one of these tautomeric forms will be indicated.

In formula (I), R_3 is preferably chosen from a hydrogen atom and a C_1 - C_4 alkyl radical optionally substituted with one or more radicals chosen from hydroxyl, C_1 - C_2 alkoxy, amino, C_1 - C_2 (mono)- or (di)alkylamino, 2-hydroxyethyl and 2-aminoethyl radicals. By way of example, R_3 represents a hydrogen atom or a methyl, ethyl or 2-hydroxyethyl radical and even more preferably: a hydrogen atom or a methyl radical.

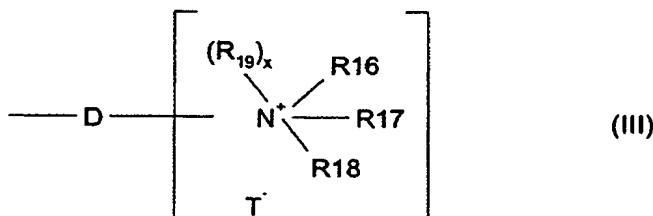
The radicals R_1 and R_2 are preferably chosen, separately, from a hydrogen atom and a C_1 - C_6 alkyl radical optionally substituted with a hydroxyl, alkoxy, amino or C_1 - C_4 (mono)- or (di)alkylamino. By way of example, R_1 and R_2 are chosen from a hydrogen atom, a methyl, ethyl, hydroxyethyl, propyl, etc. radical.

When R_1 and R_2 form, with the nitrogen atom to which they are attached, a 5- or 8-membered

heterocycle, this heterocycle is preferably chosen from pyrrolidine, piperidine, homopiperidine, piperazine, homopiperazine and optionally substituted diazepane heterocycles. By way of example, the heterocycle is
 5 chosen from pyrrolidine, 3-hydroxypyrrolidine, 3-aminopyrrolidine, 3-N,N-dimethylaminopyrrolidine, 3-acetamidopyrrolidine, 3-(methylsulphonylamino)pyrrolidine, proline, 3-hydroxyproline, piperidine, hydroxypiperidine,
 10 homopiperidine, diazepane, N-methylhomopiperazine and N-β-hydroxyethylhomopiperazine, and the addition salts thereof. Preferably, R₁ and R₂ form, with the nitrogen atoms to which they are attached, an optionally substituted pyrrolidine ring.

15 According to one particular embodiment, the compound of formula (I) is a cationic compound substituted with at least one onium radical Z, ie a cationic radical of the quaternary ammonium type.

The onium radical Z may be represented by
 20 formula (III) below



in which

- D is a covalent bond or a linear or branched C₁-C₁₄ alkylene chain which may contain one or more hetero atoms chosen from oxygen, sulphur and nitrogen, SO₂ or one or more ketone functions, the chain possibly being substituted with one or more hydroxyl, C₁-C₆ alkoxy, amino or C₁-C₄ (mono)- or (di)alkylamino radicals,
- R₁₆, R₁₇ and R₁₈, taken separately, represent a C₁-C₁₅ alkyl radical; a C₁-C₆ monohydroxyalkyl radical; a C₂-C₆ polyhydroxyalkyl radical; a (C₁-C₆)alkoxy(C₁-C₆)alkyl radical; an aryl radical; a benzyl radical; a C₁-C₆ amidoalkyl radical; a tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl radical; a C₁-C₆ aminoalkyl radical; a C₁-C₆ aminoalkyl radical in which the amine is mono- or disubstituted with a C₁-C₄ alkyl, (C₁-C₆)alkylcarbonyl, amido or (C₁-C₆)alkylsulphonyl radical; a carbamyl(C₁-C₆)alkyl radical; a (C₁-C₆)alkylcarboxy(C₁-C₆)alkyl radical; a (C₁-C₆)alkylcarbonyl(C₁-C₆)alkyl radical; an N-(C₁-C₆)alkylcarbamyl(C₁-C₆)alkyl radical;
- R₁₆, R₁₇ and R₁₈ together, in pairs, form, with the nitrogen atom to which they are attached, a 4-, 5-, 6- or 7-membered carbon-based saturated ring which may contain one or more

hetero atoms, the cationic ring possibly
being substituted with a halogen atom, a
hydroxyl radical, a C₁-C₆ alkyl radical, a
C₁-C₆ monohydroxyalkyl radical, a C₂-C₆
5 polyhydroxyalkyl radical, a C₁-C₆ alkoxy
radical, a tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl
radical, an amido radical, a carboxyl
radical, a C₁-C₆ alkylcarbonyl radical, a thio
radical, a C₁-C₆ thioalkyl radical, a
10 (C₁-C₆)alkylthio radical, an amino radical or
an amino radical mono- or disubstituted with
a (C₁-C₆)alkyl, (C₁-C₆)alkylcarbonyl, amido or
(C₁-C₆)alkylsulphonyl radical;

- R₁₉ represents a C₁-C₆ alkyl radical; a C₁-C₆
15 monohydroxyalkyl radical; a C₂-C₆
polyhydroxyalkyl radical; an aryl radical; a
benzyl radical; a C₁-C₆ aminoalkyl radical; a
C₁-C₆ aminoalkyl radical in which the amine is
mono- or disubstituted with a (C₁-C₆)alkyl,
20 (C₁-C₆)alkylcarbonyl, amido or
(C₁-C₆)alkylsulphonyl radical; a carboxy(C₁-
C₆)alkyl radical; a carbamyl(C₁-C₆)alkyl
radical; a C₁-C₆ trifluoroalkyl radical; a
tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl radical; a
25 C₁-C₆ sulphonamidoalkyl radical; a
(C₁-C₆)alkylcarboxy(C₁-C₆)alkyl radical; a
(C₁-C₆)alkylsulphonyl(C₁-C₆)alkyl radical; a

(C₁-C₆) alkylsulphonyl (C₁-C₆) alkyl radical; a
(C₁-C₆) alkylcarbonyl (C₁-C₆) alkyl radical; an
N-(C₁-C₆) alkylcarbamyl (C₁-C₆) alkyl radical; an
N-(C₁-C₆) alkylsulphonamido (C₁-C₆) alkyl
5 radical;

- x is 0 or 1,

- when x = 0, then linker arm D is
attached to the nitrogen atom
bearing the radicals R₁₆ to R₁₈,

10 - when x = 1, then two of the
radicals R₁₆ to R₁₈ form, together
with the nitrogen atom to which
they are attached, a 5-, 6- or 7-
membered saturated ring and the
15 linker arm D is linked to a carbon
atom of the saturated ring;

- T is a counterion.

According to a first variant of formula
(III), when x is equal to 0 and R₁₆, R₁₇ and R₁₈,
20 separately, are preferably chosen from a C₁-C₆ alkyl
radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄
polyhydroxyalkyl radical, a (C₁-C₆) alkoxy (C₁-C₄) alkyl
radical, a C₁-C₆ amidoalkyl radical or a
tri (C₁-C₆) alkylsilane (C₁-C₆) alkyl radical.

25 According to a second variant of formula
(III), when x is equal to 0 and R₁₆ and R₁₇ together
form an azetidine, pyrrolidine, piperidine,

homopiperidine, piperazine, homopiperazine or morpholine ring, then R₁₈ is chosen from a C₁-C₆ alkyl radical; a C₁-C₆ monohydroxyalkyl radical; a C₂-C₆ polyhydroxyalkyl radical; a C₁-C₆ aminoalkyl radical; an
5 aminoalkyl radical in which the amine is mono- or disubstituted with a (C₁-C₄)alkyl, (C₁-C₆)alkylcarbonyl, amido or (C₁-C₆)alkylsulphonyl radical; a C₁-C₆ carbamylalkyl radical; a tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl radical; a (C₁-C₆)alkylcarboxy(C₁-C₆)alkyl
10 radical; a (C₁-C₆)alkylcarbonyl(C₁-C₆)alkyl radical; an N-(C₁-C₆)alkylcarbamyl(C₁-C₆)alkyl radical.

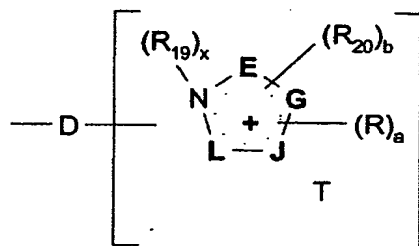
In formula (III), when x is equal to 1, R₁₉ is preferably chosen from a C₁-C₆ alkyl radical; a C₁-C₆ monohydroxyalkyl radical; a C₂-C₆ polyhydroxyalkyl
15 radical; a C₁-C₆ aminoalkyl radical; a C₁-C₆ aminoalkyl radical in which the amine is mono- or disubstituted with a (C₁-C₆)alkyl, (C₁-C₆)alkylcarbonyl, amido or (C₁-C₆)alkylsulphonyl radical; a C₁-C₆ carbamylalkyl radical; a tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl radical; a
20 (C₁-C₆)alkylcarboxy(C₁-C₆)alkyl radical; a (C₁-C₆)alkylcarbonyl(C₁-C₆)alkyl radical; an N-(C₁-C₆)alkylcarbamyl(C₁-C₆)alkyl radical; R₁₆ and R₁₇ together form an azetidine, pyrrolidine, piperidine, homopiperidine, piperazine, homopiperazine or
25 morpholine ring, and R₁₈ is then chosen from a C₁-C₆ alkyl radical; a C₁-C₆ monohydroxyalkyl radical; a C₂-C₆ polyhydroxyalkyl radical; a C₁-C₆ aminoalkyl radical; a

C₁-C₆ aminoalkyl radical in which the amine is mono- or disubstituted with a (C₁-C₄)alkyl, (C₁-C₆)alkylcarbonyl, amido or (C₁-C₆)alkylsulphonyl radical; a C₁-C₆ carbamylalkyl radical; a tri(C₁-C₆)alkylsilane(C₁-
5 C₆)alkyl radical; a (C₁-C₆)alkylcarboxy(C₁-C₆)alkyl radical; a (C₁-C₆)alkylcarbonyl(C₁-C₆)alkyl radical; an N-(C₁-C₆)alkylcarbamyl(C₁-C₆)alkyl radical.

According to one preferred embodiment, x is equal to 0, and R₁₆, R₁₇ and R₁₈ are alkyl radicals.

10 In formula (III), D is preferably a covalent bond or a C₁-C₆ alkylene chain which may be substituted.

The onium radical Z may also be represented by formula (IV)



(IV)

15

in which

- D is as defined above,
 - the ring members E, G, J and L, which may be identical or different, represent a carbon, oxygen, sulphur or nitrogen atom to form a pyrazole, imidazole, triazole, oxazole, isoxazole, thiazole or isothiazole ring,
 - a is an integer between 0 and 3 inclusive;
- 20

- b is an integer between 0 and 1 inclusive;
- a+b is an integer between 2 and 4,
- R, which may be identical or different,
represent a hydrogen or halogen atom, a
5 hydroxyl radical, a C₁-C₆ alkyl radical, a
C₁-C₆ monohydroxyalkyl radical, a C₂-C₆
polyhydroxyalkyl radical, a C₁-C₆ alkoxy
radical, a tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl
radical, an amido radical, a carboxyl
10 radical, a C₁-C₆ alkylcarbonyl radical, a thio
radical, a C₁-C₆ thioalkyl radical, a
(C₁-C₆)alkylthio radical, an amino radical, an
amino radical mono- or disubstituted with a
(C₁-C₆)alkyl, (C₁-C₆)alkylcarbonyl, amido or
15 (C₁-C₆)alkylsulphonyl radical; a C₁-C₆
monohydroxyalkyl radical or a C₂-C₆
polyhydroxyalkyl radical; a benzyl radical; a
phenyl radical optionally substituted with
one or more radicals chosen from methyl,
20 hydroxyl, amino and methoxy radicals; it
being understood that the radicals R are
borne by a carbon atom,
- R₂₀ represents a C₁-C₆ alkyl radical, a C₁-C₆
monohydroxyalkyl radical, a C₂-C₆
25 polyhydroxyalkyl radical, a
tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl radical, a
(C₁-C₆)alkoxy(C₁-C₆)alkyl radical, a C₁-C₆

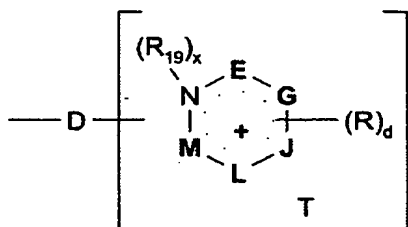
carbamylalkyl radical, a (C₁-C₆)alkylcarboxy-
 (C₁-C₆)alkyl radical or a benzyl radical; it
 being understood that the radical R₂₀ is borne
 by a nitrogen atom,

- 5 • R₁₉ is as defined above,
- x is equal to 0 or 1,
- when x = 0, the linker arm D is
 attached to the nitrogen atom,
- when x = 1, the linker arm D is
 10 attached to one of the ring members
 E, G, J or L when E, G, J or L
 represents a carbon atom,
- T is a counterion.

 Preferably, the ring members E, G, J and L
 15 form an imidazole, pyrazole, oxazole, thiazole or
 triazole ring.

 According to one particular embodiment of
 formula (III), x is equal to 0, and D is a covalent
 bond or a C₁-C₄ alkylene chain which may be substituted.

20 The onium radical Z may be represented by
 formula (V)



(V)

in which

- D, R and R₁₉ are as defined above,
- the ring members E, G, J, L and M, which may be identical or different, represent a carbon or nitrogen atom and form a ring chosen from pyridine, pyrimidine, pyrazine, triazine and pyridazine rings,
- d is an integer between 3 and 5 inclusive,
- x is equal to 0 or 1,
 - when x = 0, the linker arm D is attached to the nitrogen atom,
 - when x = 1, the linker arm D is attached to one of the ring members E, G, J, L or M, when E, G, J, L or M represents a carbon atom,
- T represents a counterion.

Preferably, the ring members E, G, J, L and M form, with the nitrogen of the ring, a ring chosen from pyridine, pyrimidine, pyridazine and pyrazine rings.

According to one variant of formula (V), x is equal to 0 and R is chosen from a hydroxyl radical, a C₁-C₆ alkyl radical, a C₁-C₆ monohydroxyalkyl radical, a C₂-C₆ polyhydroxyalkyl radical, a C₁-C₆ alkoxy radical, a tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl radical, an amido radical, a C₁-C₆ alkylcarbonyl radical, an amino radical, an amino radical mono- or disubstituted with a (C₁-C₆)alkyl, (C₁-C₆)alkylcarbonyl, amido or (C₁-C₆)alkylsulphonyl radical; a C₁-C₆ monohydroxyalkyl

radical or a C₂-C₆ polyhydroxyalkyl radical; it being understood that the radicals R are borne by a carbon atom.

According to another variant of formula (V),
5 x is equal to 1, R₁₉ is chosen from a C₁-C₆ alkyl radical; a C₁-C₆ monohydroxyalkyl radical; a C₂-C₆ polyhydroxyalkyl radical; a C₁-C₆ aminoalkyl radical, a C₁-C₆ aminoalkyl radical in which the amine is mono- or disubstituted with a (C₁-C₆)alkyl, (C₁-C₆)alkylcarbonyl,
10 amido or (C₁-C₆)alkylsulphonyl radical; a C₁-C₆ carbamylalkyl radical; a tri(C₁-C₆)alkylsilane(C₁-C₆)-alkyl radical; a (C₁-C₆)alkylcarbonyl(C₁-C₆)alkyl radical; an N-(C₁-C₆)alkylcarbamyl(C₁-C₆)alkyl radical;
R is chosen from a hydroxyl radical, a C₁-C₆ alkyl
15 radical, a C₁-C₆ monohydroxyalkyl radical, a C₂-C₆ polyhydroxyalkyl radical, a C₁-C₆ alkoxy radical, a tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl radical, an amido radical, a C₁-C₆ alkylcarbonyl radical, an amino radical or an amino radical mono- or disubstituted with a
20 (C₁-C₆)alkyl, (C₁-C₆)alkylcarbonyl, amido or (C₁-C₆)alkylsulphonyl radical.

In one preferred embodiment, R₁₉ is a C₁-C₄ alkyl radical which may be substituted, and R is a hydrogen radical or a C₁-C₄ alkyl radical which may be
25 substituted.

When the compound of formula (I) is a cationic compound substituted with a radical Z,

preferably, at least one of the radicals R_1 and R_2 represents an onium radical Z. According to one particular embodiment, R_1 and R_2 form a ring of formula (II) in which R' is an onium radical Z, preferably with
5 Y equal to $NR'_6R'_7$.

In formula (I), W_1 in particular represents 5-aminopyrazole, 5-hydroxypyrazole, pyrazolo[1,5-b]pyridine, pyrazolo[1,5-a]pyrimidine, pyrazolo[3,2-c]triazole, pyrazolo[1,5-b]triazole,
10 aminopyrimidine, triaminopyrimidine, hydroxyaminopyrimidine, 2-aminopyridine, indoline and indole radicals.

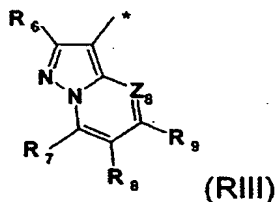
According to one particular embodiment, W_1 is chosen from the 5-aminopyrazole and 5-hydroxypyrazole
15 radicals of formula (R1).

In this case, W_1 is preferably chosen from 5-aminopyrazole and 5-hydroxypyrazole radicals in which R_6 and R_{11} , which may be identical or different, are chosen from a hydrogen atom; a linear or branched C_1 - C_{10}
20 hydrocarbon-based chain, which can form one or more 4- to 8-membered carbon-based rings, and which may be saturated or unsaturated, at one or more of the carbon atoms of the carbon-based chain of which may be replaced with an oxygen, nitrogen or sulphur atom or
25 with an SO_2 group, and the carbon atoms of which may be, independently of each other, substituted with one or more halogen atoms or hydroxyl, amino, carboxyl,

sulphonic or thiol radicals; the radicals R_6 to R_{12} not comprising a peroxide bond or diazo or nitroso radicals and the radical R_{11} not being linked directly to the nitrogen atom via an oxygen, sulphur or nitrogen atom.

5 According to one particularly preferred embodiment of (R_1), R_6 and R_{11} are chosen, independently, from a hydrogen atom and a linear or branched C_1 - C_4 hydrocarbon-based chain, which can form one or more 5- or 6-membered carbon-based rings, and
10 which may be saturated or unsaturated, the carbon atoms of which may be, independently of each other, substituted with one or more halogen atoms or hydroxyl or amino radicals.

 According to another particular embodiment,
15 W_1 represents



R_6 , R_7 , R_8 , R_9 and Z_8 being as defined above.

 In this particular case, W_1 may be a pyrazolo[1,5-b]pyridine radical in which R_6 , R_7 , R_8 , R_9
20 and R_{15} , which may be identical or different, are chosen from

- a hydrogen atom,
- a linear or branched C_1 - C_{10} hydrocarbon-based chain, which may form one or more 4- to 8-
25 membered carbon-based rings, and which may be

5 saturated or unsaturated, one or more carbon
atoms of the carbon-based chain of which may
be replaced with an oxygen, nitrogen or
sulphur atom or with an SO₂ group, and the
carbon atoms of which may be, independently
of each other, substituted with one or more
halogen atoms or hydroxyl, amino, carboxyl,
sulphonic or thiol radicals; the radicals not
comprising a peroxide bond or diazo or
10 nitroso radicals,

- hydroxyl or amino radicals, the amine
possibly being substituted with a linear or
branched C₁-C₄ hydrocarbon-based chain, which
can form one or more 5- or 6-membered carbon-
15 based rings, and which may be saturated or
unsaturated, the carbon atoms may be,
independently of each other, substituted with
one or more halogen atoms or hydroxyl or
amino radicals.

20 In this particular case, W₁ may also be a
pyrazolo[1,5-b]pyridine radical in which R₆, R₇, R₈, R₉
and R₁₅, which may be identical or different, are chosen
from:

- a hydrogen atom,
- 25 • a linear or branched C₁-C₁₀ hydrocarbon-based
chain, which can form one or more 4- to 8-
membered carbon-based rings, and which may be

5 saturated or unsaturated, one or more carbon
atoms of the carbon-based chain of which may
be replaced with an oxygen, nitrogen or
sulphur atom or with an SO₂ group, and the
carbon atoms of which may be, independently
of each other, substituted with one or more
halogen atoms or hydroxyl, amino, carboxyl,
sulphonic or thiol radicals; the radicals not
comprising a peroxide bond or diazo or
10 nitroso radicals,

- hydroxyl or amino radicals, the amine possibly
being substituted with a linear or branched
C₁-C₄ hydrocarbon-based chain, which can form
one or more 6-membered carbon-based rings,
15 and which may be saturated or unsaturated,
the carbon atoms may be, independently of
each other, substituted with one or more
halogen atoms or hydroxyl or amino radicals.

In this particular case, W₁ may also be a
20 pyrazolo[1,5-b]pyridine radical in which R₆, R₇, R₈, R₉
and R₁₅, which may be identical or different, are chosen
from:

- a hydrogen atom,
- a linear or branched C₁-C₁₀ hydrocarbon-based
25 chain, which can form one or more 4- to 8-
membered carbon-based rings, and which may be
saturated or unsaturated, and the carbon

atoms of which may be, independently of each other, substituted with one or more halogen atoms or hydroxyl, amino, monosubstituted or disubstituted amino, C₁-C₄ alkoxy, C₁-C₄ thioether, carboxyl, sulphonic or thiol radicals;

- hydroxyl or amino radicals, the amine possibly being substituted with a linear or branched C₁-C₄ hydrocarbon-based chain, which can form one or more 5- or 6-membered carbon-based rings, and which may be saturated or unsaturated, the carbon atoms may be, independently of each other, substituted with one or more halogen atoms or hydroxyl or amino radicals.

When W₁ is a pyrazolo[1,5-b]pyridine radical, the radicals R₆, R₇, R₈, R₉ and R₁₅ are preferably chosen from a hydrogen atom, a linear or branched C₁-C₄ hydrocarbon-based chain which may be saturated or unsaturated, the carbon atoms may be, independently of each other, substituted with one or more halogen atoms or hydroxyl or amino radicals.

W₁ may also be a pyrazolo[1,5-a]pyrimidine radical in which R₇ and R₉ are chosen from a hydrogen atom, a linear or branched C₁-C₆ alkyl radical; a C₁-C₆ monohydroxyalkyl radical; a C₂-C₆ polyhydroxyalkyl radical; a C₁-C₆ aminoalkyl radical or a C₁-C₆

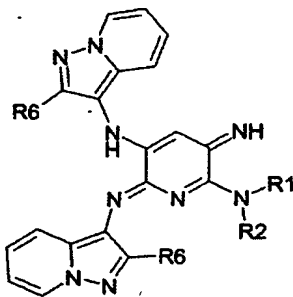
aminoalkyl radical in which the amine is mono- or
disubstituted with a (C₁-C₆)alkyl or
(C₁-C₆)alkylcarbonyl radical, a hydroxyl or amino
radical, the amino possibly being substituted with a
5 linear or branched C₁-C₁₀ hydrocarbon-based chain, which
can form one or more 5- or 6-membered carbon-based
rings which may be saturated or unsaturated, the carbon
atoms may be, independently of each other, substituted
with one or more halogen atoms or hydroxyl or amino
10 radicals; R₆ and R₈ are chosen from a hydrogen atom, a
linear or branched C₁-C₆ alkyl radical; a C₁-C₆
monohydroxyalkyl radical; a C₂-C₆ polyhydroxyalkyl
radical; a C₁-C₆ aminoalkyl radical or a C₁-C₆
aminoalkyl radical in which the amine is mono- or
15 disubstituted with a (C₁-C₆)alkyl or
(C₁-C₆)alkylcarbonyl radical. In this case, R₇ and R₉
are preferably chosen from a hydrogen atom; a linear or
branched C₁-C₄ alkyl radical; a C₁-C₄ monohydroxyalkyl
radical; a C₂-C₄ polyhydroxyalkyl radical; a C₁-C₄
20 aminoalkyl radical or a C₁-C₄ aminoalkyl in which the
amine is mono- or disubstituted with a (C₁-C₂)alkyl
radical, a hydroxyl or amino radical, the amino
possibly being substituted with a linear or branched
C₁-C₄ hydrocarbon-based chain, the carbon atoms may be,
25 independently of each other, substituted with one or
more hydroxyl or amino radicals, and R₆ and R₈ are
preferably chosen from a hydrogen atom, a linear or

branched C₁-C₄ alkyl radical; a C₁-C₄ monohydroxyalkyl
radical; a C₂-C₄ polyhydroxyalkyl radical; a C₁-C₄
aminoalkyl radical or a C₁-C₄ aminoalkyl radical in
which the amine is mono- or disubstituted with a
5 (C₁-C₂)alkyl radical; a C₁-C₂ alkoxy radical.

According to one particularly preferred
embodiment, W₁ is a pyrazolopyridine or
pyrazolopyrimidine derivative in which R₆, R₇, R₈ and R₉
are preferably chosen from a hydrogen atom; a C₁-C₄
10 alkyl radical; an amino radical; a C₁-C₄ mono- or
dialkylamino radical; a C₁-C₄ hydroxyalkyl radical or a
C₁-C₂ alkoxy radical.

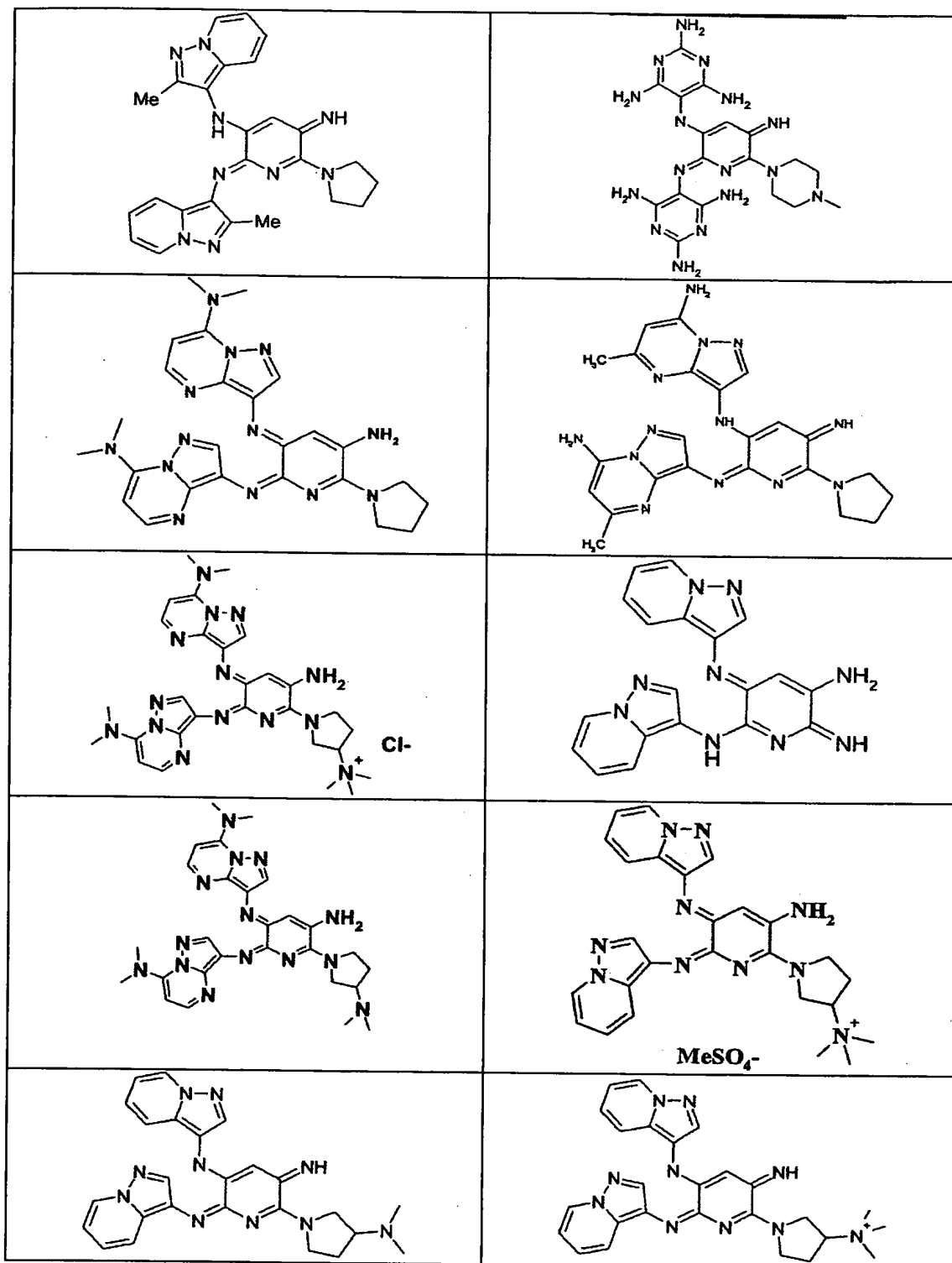
The compound of formula (I) may be
represented by the following formula

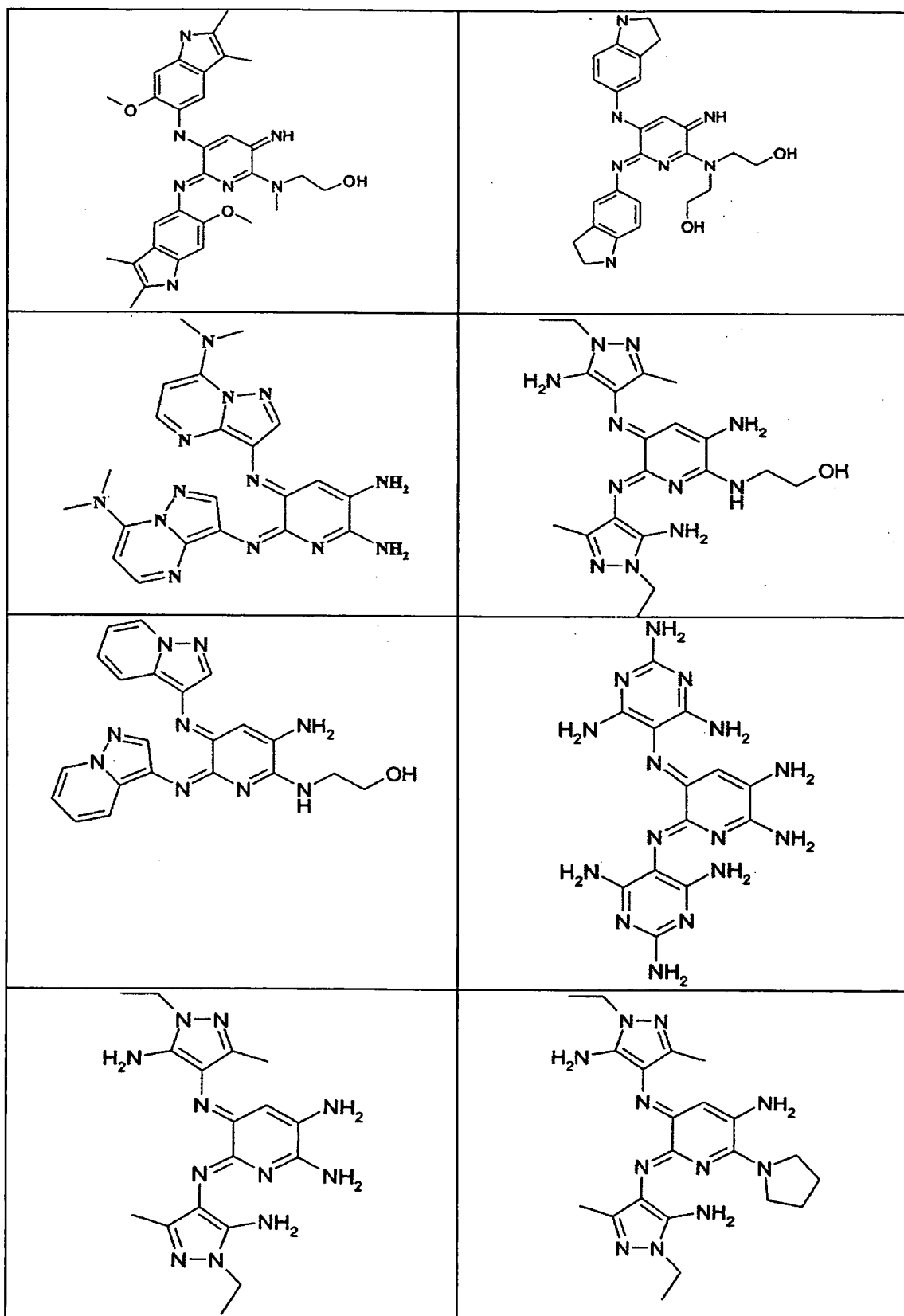
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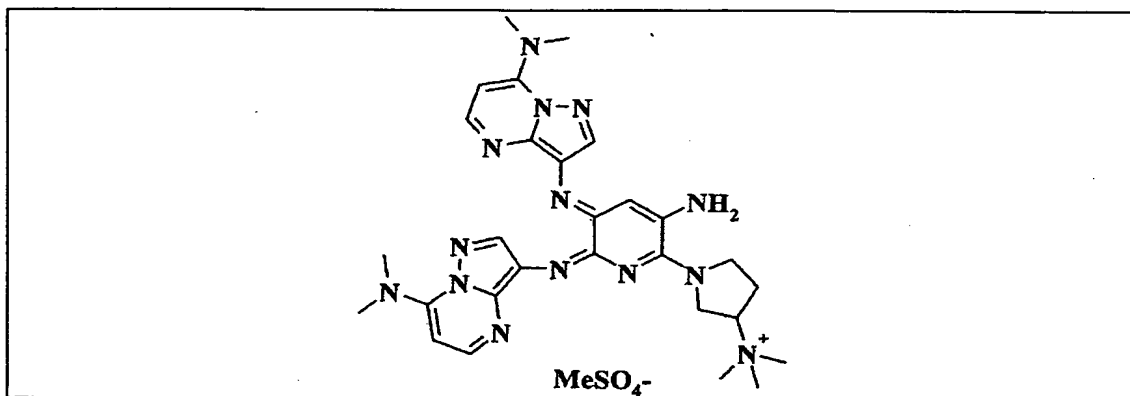


in which R₁, R₂ and R₆ are as defined above.

By way of example, the compounds of formula
20 (I) may be cited







The composition of the invention preferably contains an amount of compound of formula (I) of between 0.01% and 10% by weight and preferably between
5 0.1% to 5% by weight.

The dye composition in accordance with the invention may also contain direct dyes other than the compounds of formula (I). These direct dyes that are useful according to the invention are chosen, for
10 example, from neutral, acidic or cationic nitrobenzene direct dyes, neutral, acidic or cationic azo direct dyes, quinone direct dyes and in particular neutral, acidic or cationic anthraquinone direct dyes, azine direct dyes, triarylmethane direct dyes, indoamine
15 direct dyes and natural direct dyes.

Among the benzenic direct dyes that may be used according to the invention, mention may be made, in a nonlimiting manner, of the following compounds:

- 1,4-diamino-2-nitrobenzene
- 20 - 1-amino-2-nitro-4-β-hydroxyethylaminobenzene
- 1-amino-2-nitro-4-bis(β-hydroxyethyl)aminobenzene

- 1,4-bis(β -hydroxyethylamino)-2-nitrobenzene
- 1- β -hydroxyethylamino-2-nitro-4-bis(β -hydroxyethylamino)benzene
- 1- β -hydroxyethylamino-2-nitro-4-aminobenzene
- 5 - 1- β -hydroxyethylamino-2-nitro-4-(ethyl)(β -hydroxyethyl)aminobenzene
- 1-amino-3-methyl-4- β -hydroxyethylamino-6-nitrobenzene
- 1-amino-2-nitro-4- β -hydroxyethylamino-5-chlorobenzene
- 1,2-diamino-4-nitrobenzene
- 10 - 1-amino-2- β -hydroxyethylamino-5-nitrobenzene
- 1,2-bis(β -hydroxyethylamino)-4-nitrobenzene
- 1-amino-2-tris(hydroxymethyl)methylamino-5-nitrobenzene
- 1-hydroxy-2-amino-5-nitrobenzene
- 15 - 1-hydroxy-2-amino-4-nitrobenzene
- 1-hydroxy-3-nitro-4-aminobenzene
- 1-hydroxy-2-amino-4,6-dinitrobenzene
- 1- β -hydroxyethyloxy-2- β -hydroxyethylamino-5-nitrobenzene
- 20 - 1-methoxy-2- β -hydroxyethylamino-5-nitrobenzene
- 1- β -hydroxyethyloxy-3-methylamino-4-nitrobenzene
- 1- β , γ -dihydroxypropyloxy-3-methylamino-4-nitrobenzene
- 1- β -hydroxyethylamino-4- β , γ -dihydroxypropyloxy-2-nitrobenzene
- 25 - 1- β , γ -dihydroxypropylamino-4-trifluoromethyl-2-nitrobenzene
- 1- β -hydroxyethylamino-4-trifluoromethyl-2-nitrobenzene

- 1- β -hydroxyethylamino-3-methyl-2-nitrobenzene
- 1- β -aminoethylamino-5-methoxy-2-nitrobenzene
- 1-hydroxy-2-chloro-6-ethylamino-4-nitrobenzene
- 1-hydroxy-2-chloro-6-amino-4-nitrobenzene
- 5 - 1-hydroxy-6-bis(β -hydroxyethyl)amino-3-nitrobenzene
- 1- β -hydroxyethylamino-2-nitrobenzene
- 1-hydroxy-4- β -hydroxyethylamino-3-nitrobenzene.

Among the azo direct dyes that may be used according to the invention, mention may be made of the
10 cationic azo dyes described in patent applications WO 95/15144, WO-95/01772 and EP-714 954, the content of which forms an integral part of the invention.

Among these compounds that may be mentioned most particularly are the following dyes:

- 15 - 1,3-dimethyl-2-[[4-(dimethylamino)phenyl]azo]-1H-imidazolium chloride,
- 1,3-dimethyl-2-[(4-aminophenyl)azo]-1H-imidazolium chloride,
- 1-methyl-4-[(methylphenylhydrazono)methyl]pyridinium
- 20 methyl sulphate.

Among the azo direct dyes that may also be mentioned are the following dyes, described in the Color Index International 3rd edition:

- Disperse Red 17
- 25 - Acid Yellow 9
- Acid Black 1
- Basic Red 22

- Basic Red 76
- Basic Yellow 57
- Basic Brown 16
- Acid Yellow 36
- 5 - Acid Orange 7
- Acid Red 33
- Acid Red 35
- Basic Brown 17
- Acid Yellow 23
- 10 - Acid Orange 24
- Disperse Black 9.

Mention may also be made of 1-(4'-aminodiphenylazo)-2-methyl-4-bis(β -hydroxyethyl)aminobenzene and 4-hydroxy-3-(2-methoxyphenylazo)-1-naphthalenesulphonic acid.

- Among the quinone direct dyes that may be mentioned are the following dyes:
- Disperse Red 15
 - Solvent Violet 13
 - 20 - Acid Violet 43
 - Disperse Violet 1
 - Disperse Violet 4
 - Disperse Blue 1
 - Disperse Violet 8
 - 25 - Disperse Blue 3
 - Disperse Red 11
 - Acid Blue 62

- Disperse Blue 7
- Basic Blue 22
- Disperse Violet 15
- Basic Blue 99

5 and also the following compounds:

- 1-N-Methylmorpholiniumpropylamino-4-hydroxyanthraquinone
- 1-Aminopropylamino-4-methylaminoanthraquinone
- 1-Aminopropylaminoanthraquinone
- 10 - 5- β -Hydroxyethyl-1,4-diaminoanthraquinone
- 2-Aminoethylaminoanthraquinone
- 1,4-Bis(β , γ -dihydroxypropylamino)anthraquinone.

Among the azine dyes that may be mentioned are the following compounds:

- 15 - Basic Blue 17
- Basic Red 2.

Among the triarylmethane dyes, mention may be made of the following compounds:

- Basic Green 1
- 20 - Acid Blue 9
- Basic Violet 3
- Basic Violet 14
- Basic Blue 7
- Acid Violet 49
- 25 - Basic Blue 26
- Acid Blue 7.

Among the indoamine dyes, mention may be made of the following compounds:

- 2- β -Hydroxyethylamino-5-[bis(β -4'-hydroxyethyl)amino]anilino-1,4-benzoquinone
- 5 - 2- β -Hydroxyethylamino-5-(2'-methoxy-4'-amino)anilino-1,4-benzoquinone
- 3-N-(2'-Chloro-4'-hydroxy)phenylacetyl-amino-6-methoxy-1,4-benzoquinone imine
- 3-N-(3'-Chloro-4'-methylamino)phenylureido-6-methyl-10 1,4-benzoquinone imine
- 3-[4'-N-(Ethyl, carbamylmethyl)amino]phenylureido-6-methyl-1,4-benzoquinone imine.

Among the natural direct dyes that may be used according to the invention, mention may be made of
15 lawsone, juglone, alizarin, purpurin, carminic acid, kermesic acid, purpurogallin, protocatechaldehyde, indigo, isatin, curcumin, spinulosin and apigenidin. It is also possible to use extracts or decoctions containing these natural dyes, and especially henna-
20 based poultices or extracts.

The direct dye(s) preferably represent(s) from 0.001% to 20% by weight approximately relative to the total weight of the ready-to-use composition, and even more preferably from 0.005% to 10% by weight
25 approximately.

The composition of the present invention may also contain oxidation bases and couplers conventionally used for oxidation dyeing.

Examples that may be mentioned include para-
5 phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof.

The couplers are, for example, meta-phenylenediamine couplers, meta-aminophenol couplers,
10 meta-diphenol couplers, naphthalene-based couplers and heterocyclic couplers, and the addition salts thereof.

When they are present, the bases and couplers are each generally present in an amount of between 0.001% and 10% by weight approximately and preferably
15 between 0.005% and 6% by weight relative to the total weight of the dye composition.

The medium that is suitable for dyeing, also known as the dye support, generally consists of water or of a mixture of water and of at least one organic
20 solvent to dissolve the compounds that would not be sufficiently water-soluble. Examples of organic solvents that may be mentioned include C₁-C₄ lower alkanols, such as ethanol and isopropanol; polyols and polyol ethers, for instance 2-butoxyethanol, propylene
25 glycol, propylene glycol monomethyl ether and diethylene glycol monoethyl ether and monomethyl ether,

and also aromatic alcohols, for instance benzyl alcohol or phenoxyethanol, and mixtures thereof.

For dyeing human keratin fibres, the dyeing medium is a suitable cosmetic medium.

5 The solvents may be present in proportions preferably of between 1% and 40% by weight approximately and even more preferably between 5% and 30% by weight approximately relative to the total weight of the dye composition.

10 The dye composition in accordance with the invention may also contain various adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof,
15 anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, mineral or organic thickeners, and in particular anionic, cationic, nonionic and amphoteric polymeric associative thickeners, antioxidants, penetrating agents,
20 sequestering agents, fragrances, buffers, dispersants, conditioners, for instance volatile or non-volatile, modified or unmodified silicones, film-forming agents, ceramides, preserving agents and opacifiers.

 The above adjuvants are generally present in
25 an amount for each one of between 0.01% and 20% by weight relative to the weight of the composition.

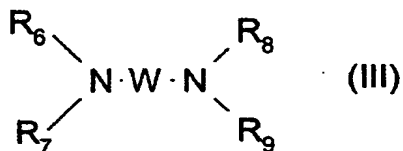
Needless to say, a person skilled in the art will take care to select this or these optional additional compound(s) such that the advantageous properties intrinsically associated with the oxidation dye composition in accordance with the invention are not, or are not substantially, adversely affected by the envisaged addition(s).

The pH of the dye composition in accordance with the invention is generally between 3 and 12 approximately and preferably between 5 and 11 approximately.

It may be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres or using standard buffer systems.

Among the acidifying agents that may be mentioned, for example, are mineral or organic acids, for instance hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids, for instance acetic acid, tartaric acid, citric acid or lactic acid, and sulphonic acids.

Among the basifying agents that may be mentioned, for example, are aqueous ammonia, alkali metal carbonates, alkanolamines such as mono-, di- or triethanolamine and also derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (III) below:



in which W is a propylene residue optionally
5 substituted with a hydroxyl group or a C₁-C₄ alkyl
radical; R₆, R₇, R₈ and R₉, which may be identical or
different, represent a hydrogen atom or a C₁-C₄ alkyl or
C₁-C₄ hydroxyalkyl radical.

The dye composition according to the
10 invention may be in various forms, such as in the form
of liquids, creams or gels, or in any other form that
it suitable for dyeing keratin fibres, and especially
human hair.

A subject of the invention is also a process
15 of direct dyeing which comprises the application of a
dye composition containing a dye of formula (I) as
defined above to keratin fibres. After an action time,
the keratin fibres are rinsed, allowing the coloured
fibres to show. The action time is generally between 3
20 and 50 minutes approximately and preferably 5 to
30 minutes approximately.

When the dye composition comprises an
oxidation base and/or a coupler, the dye composition
may then contain an oxidizing agent. The oxidizing
25 agents conventionally used for the oxidation dyeing of
keratin fibres are, for example, hydrogen peroxide,

urea peroxide, alkali metal bromates, persalts such as
perborates and persulphates, peracids and oxidase
enzymes, among which mention may be made of
peroxidases, 2-electron oxidoreductases such as
5 uricases, and 4-electron oxygenases, for instance
laccases. Hydrogen peroxide is particularly preferred.

The oxidizing agent may be added to the
composition just at the time of use, or it may be used
starting with an oxidizing composition containing it,
10 which is applied simultaneously or sequentially to the
composition of the invention. The oxidizing composition
may also contain various adjuvants conventionally used
in compositions for dyeing the hair and as defined
above.

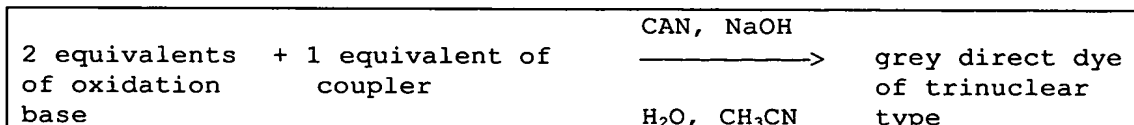
15 The pH of the oxidizing composition
containing the oxidizing agent is such that, after
mixing with the dye composition, the pH of the
resulting composition applied to the keratin fibres
preferably ranges between 3 and 12 approximately and
20 even more preferably between 5 and 11. It may be
adjusted to the desired value using acidifying or
basifying agents usually used in the dyeing of keratin
fibres and as defined above.

The composition that is finally applied to
25 the keratin fibres may be in various forms, such as in
the form of liquids, creams or gels or in any other

form that is suitable for dyeing keratin fibres, and especially human hair.

The compounds of the invention of formula (I) may be prepared in the following way:

5



The term "oxidation base" means the heterocyclic oxidation bases conventionally used in dyeing, which can, after reaction with the coupler, form a radical W_1 . The coupler used is a 2,3-diaminopyridine coupler substituted in position 6 with a leaving group such as an alkoxy, a halogen atom, an aryloxy, $-\text{OSO}_2\text{R}$, a radical $-\text{OCOR}$, or a $\text{C}_1\text{-C}_3$ trifluoroalkoxy radical, with R representing an alkyl radical.

Heterocyclic oxidation bases that may be mentioned include pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

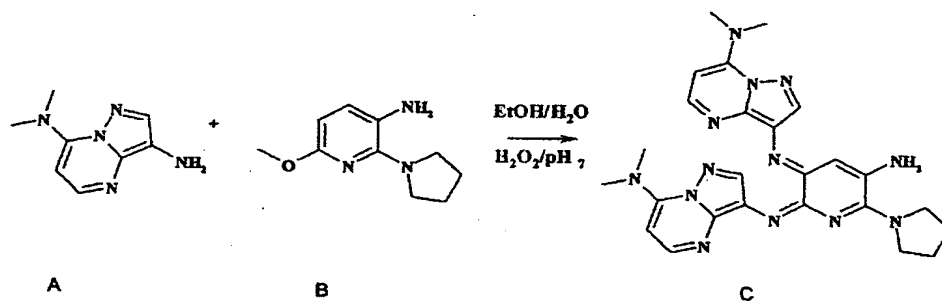
According to one particular embodiment, the base and the coupler are mixed with a solvent, for example acetonitrile. A base, for example sodium hydroxide, and CAN are added to this mixture. After (a period of) stirring, water is added to the reaction medium. The aqueous phase is extracted, for example with ethyl acetate. The organic phase is removed. The

aqueous phase is re-extracted, for example with butanol. The butanol phase is then dried, filtered and then concentrated and purified.

The examples that follow serve to illustrate the invention without, however, being limiting in nature.

EXAMPLES

Example 1: Preparation of a compound of formula:



3-Amino-7-diethylaminopyrazolopyrimidine (A: 0.440 g), 2-pyrrolidino-3-amino-6-methoxypyridine (B: 0.386 g), ethanol/water ((60/40), 40 g), H₂O₂ (20 vol., 50 g) and a buffer at pH 7 (10 g of buffer: KH₂PO₄ 13.6 g; K₂HPO₄ 26.1 g and water qs 100 ml) are mixed together and stirred at room temperature for 1 hour. The reaction mixture is then precipitated and the dye obtained (C) is purified by column chromatography.

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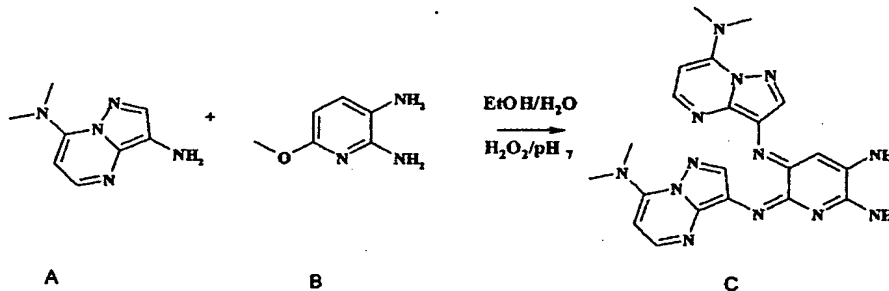
NMR (¹H CD₃OD, 400 MHz), 3.18 ppm (s, 12H); 3.97 ppm (s, 4H); 6.21 ppm (s, 1H); 6.27 ppm (s, 1H); 6.62 ppm (d,

1H); 6.71 ppm (d, 1H); 7.95 ppm (s, 1H); 8.39 ppm (d, 1H); 8.41 ppm (d, 1H); 8.83 ppm (s, 1H)

ESI+/MS M=511 (2 exchangeable protons)

5 MS/MS m/z=485 [M+H-HCN]⁺; m/z=350 [M+H-C₈H₁₀N₄]⁺ and m/z=323 [M+H-HCN-C₈H₁₀N₄]⁺ and m/z=176 [C₈N₅H₁₁-H]⁺

Example 2: Preparation of a compound of formula:



10

0.327 g of 3-amino-7-diethylaminopyrazolo-pyrimidine (A: 1.31 mmol; 2 eq.) and 0.138 g of 2,3-diamino-6-methoxypyridine (B: 0.65 mmol; 1 eq.) are dissolved in 80 ml of absolute ethanol. 8 ml of 6% aqueous hydrogen peroxide solution are then added and stirring is continued at room temperature. After one week, the mixture is filtered and the black dye (C) is recovered.

20

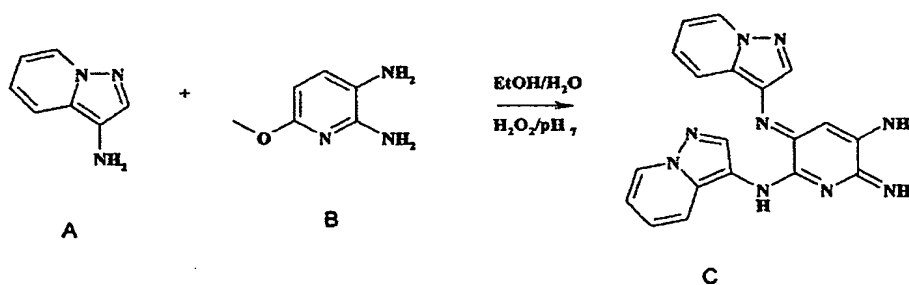
NMR (¹H, DMSO-d₆, 400 MHz): 3.14 ppm (s, 6H); 3.20 ppm (s, 6H); 6.34 ppm (s, 1H); 6.70-6.66 (2d, 2H); 8.13 ppm

(s, 1H); 8.68-8.63 ppm (2d, 2H); 9.11 (s, 1H); 10.21
(broad s, 1H exchangeable).

Mass (ES⁺): m/z: 458 (MH⁺).

5

Example 3: Preparation of a compound of formula:

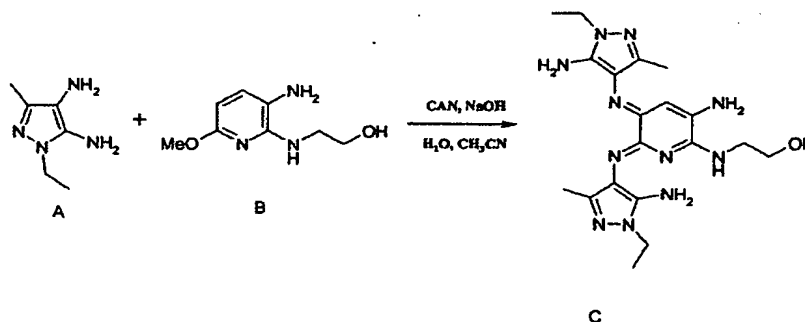


10 0.222 g of 3-aminopyrazolopyridine (A:
1.31 mmol; 2 eq.) and 0.138 g of 2,3-diamino-6-
methoxypyridine (B: 0.65 mmol; 1 eq.) are dissolved in
80 ml of absolute ethanol. 8 ml of 6% aqueous hydrogen
peroxide solution are then added and stirring is
15 continued at room temperature. After one week, the
mixture is filtered and the solid dye (C) is recovered.

NMR (¹H DMSO-d₆, 400 MHz): 5.98 ppm (s, 1H); 7.12-7.04
(2dd, 2H); 7.37 ppm (dd, 1H); 7.52-7.49 ppm (dd, 1H);
20 7.70-7.68 ppm (d, 1H); 8.29 ppm (s, 1H); 8.52-8.50 ppm
(d, 1H); 8.80-8.75 ppm (2dd, 2H); 9.22 ppm (s, 1H);
9.54 ppm (broad s, 2H exchangeable); 10.66 (broad s, 1H
exchangeable).

Mass (ES⁺): m/z: 370 (MH⁺)

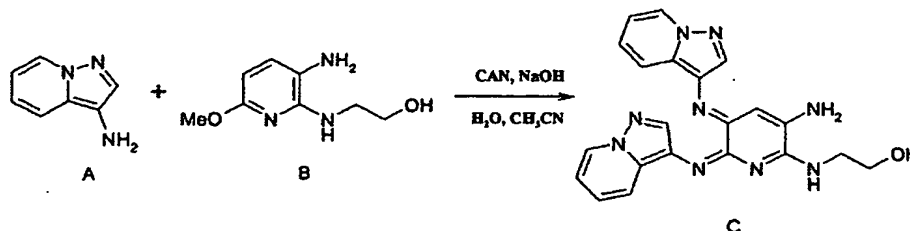
Example 4: Preparation of a compound of formula:



0.097 g of **A** (0.45 mmol; 2 eq.) and 0.050 g of **B** (0.22 mmol; 1 eq.) are placed in 10 ml of acetonitrile. 338 mg of 35% sodium hydroxide diluted in 10 ml of water are then added, immediately followed by 499 mg of CAN. The solution turns a grey-blue colour within a few minutes. After stirring for 4 hours, 100 ml of water are added. The aqueous phase is extracted with ethyl acetate. The organic phase is removed. The aqueous phase is re-extracted with butanol. The butanol phase is then dried over sodium sulphate, filtered and then concentrated. The product is taken up in ethanol (2 ml) and then reprecipitated in diisopropyl ether. A black powder is obtained (C: m = 0.081 g).

Mass (ES⁺): m/z: 428 (MH⁺)

Example 5: Preparation of a compound of formula:



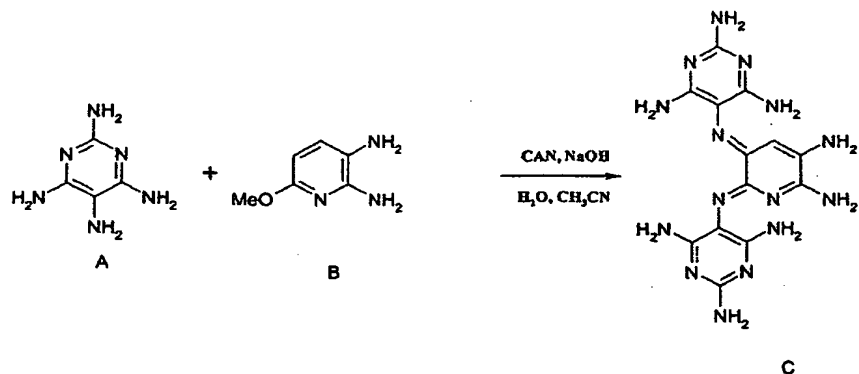
5 0.169 g of A (0.45 mmol; 2 eq.) and 0.050 g
of B (0.22 mmol; 1 eq.) are placed in 10 ml of
acetonitrile. 338 mg of 35% sodium hydroxide diluted in
10 ml of water are then added, immediately followed by
499 mg of CAN (Cerium (IV) Ammonium Nitrate:
10 $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$).

The solution turns a grey colour within a few
minutes. After stirring for 4 hours, 100 ml of water
are added. The aqueous phase is extracted with ethyl
acetate. The organic phase is removed. The aqueous
15 phase is re-extracted with butanol. The butanol phase
is then dried over sodium sulphate, filtered and then
concentrated. The product is taken up in ethanol (2 ml)
and then reprecipitated in diisopropyl ether. A black
powder is obtained (C).

20

Mass (ES⁺): m/z: 414 (MH⁺)

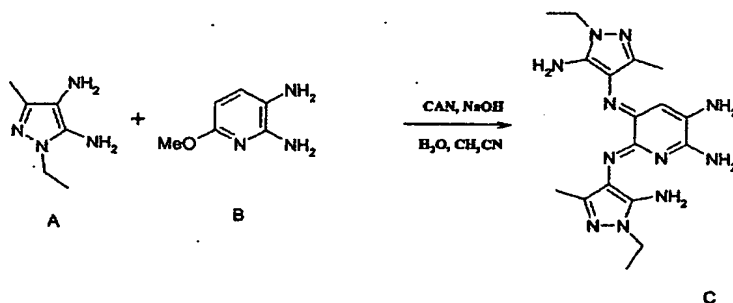
Example 6: Preparation of a compound of formula:



5 0.238 g of A (0.45 mmol; 2 eq.) and 0.050 g
 of B (0.22 mmol; 1 eq.) are placed in 10 ml of
 acetonitrile. 338 mg of 35% sodium hydroxide diluted in
 10 ml of water are then added, immediately followed by
 499 mg of CAN. The solution turns a grey colour within
 10 a few minutes. After stirring for 4 hours, 100 ml of
 water are added. The aqueous phase is extracted with
 ethyl acetate. The organic phase is removed. The
 aqueous phase is re-extracted with butanol. The butanol
 phase is then dried over sodium sulphate, filtered and
 15 then concentrated. The product is taken up in ethanol
 (2 ml) and then reprecipitated in diisopropyl ether. A
 black powder is obtained (C).

Mass (ES⁺): m/z: 384 (MH⁺)

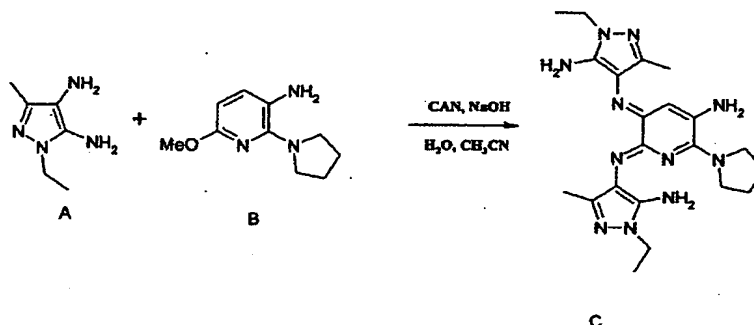
Example 7: Preparation of a compound of formula:



5 0.097 g of A (0.45 mmol; 2 eq.) and 0.050 g
 of B (0.22 mmol; 1 eq.) are placed in 10 ml of
 acetonitrile. 338 mg of 35% sodium hydroxide diluted in
 10 ml of water are then added, immediately followed by
 499 mg of CAN. The solution turns a grey-blue colour
 10 within a few minutes. After stirring for 4 hours,
 100 ml of water are added. The aqueous phase is
 extracted with ethyl acetate. The organic phase is
 removed. The aqueous phase is re-extracted with
 butanol. The butanol phase is then dried over sodium
 15 sulphate, filtered and then concentrated. The product
 is taken up in ethanol (2 ml) and then reprecipitated
 in diisopropyl ether. A black powder is obtained (C).

Mass (ES⁺): m/z: 384 (MH⁺)

Example 8: Preparation of a compound of formula:



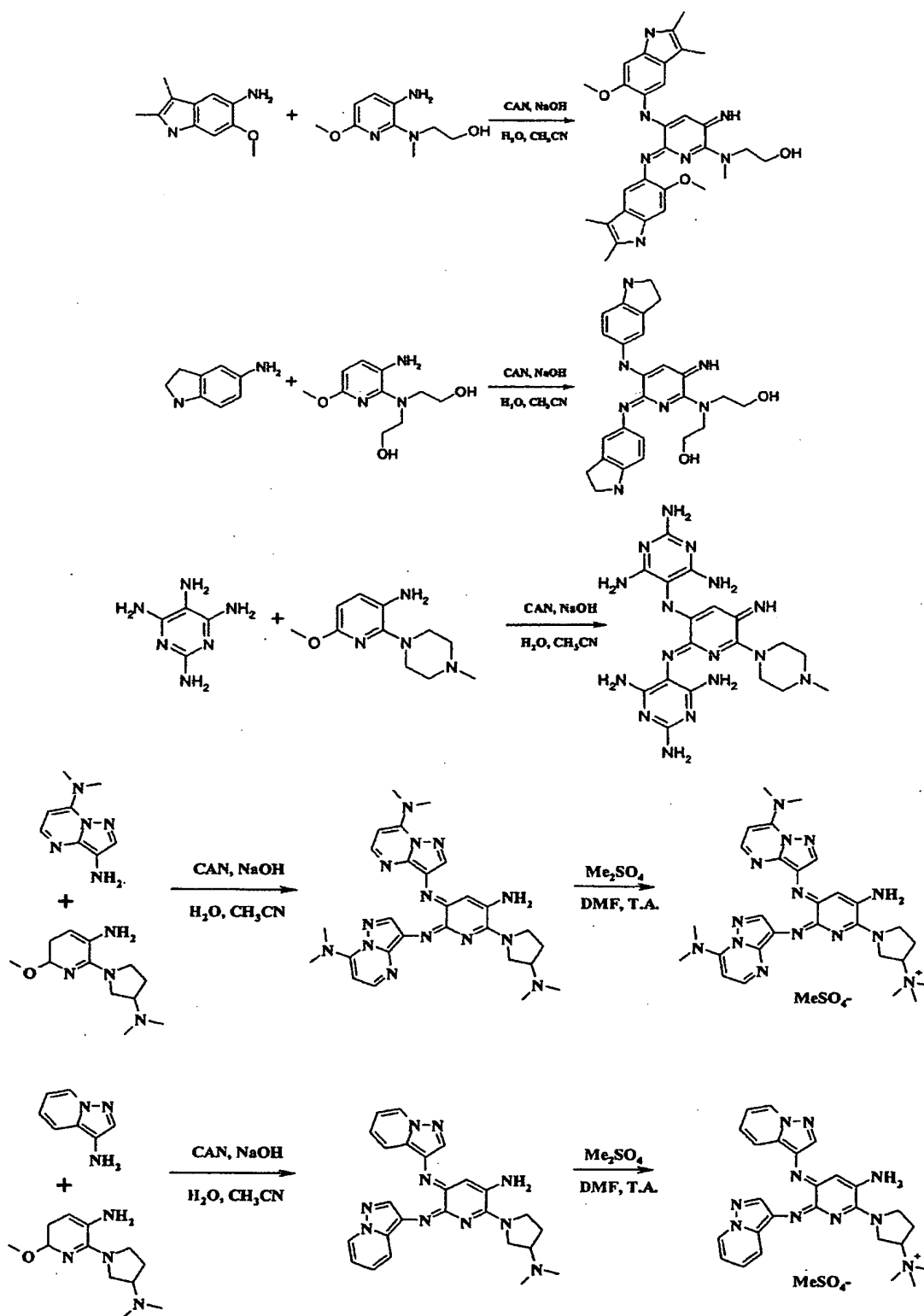
5 0.097 g of A (0.45 mmol; 2 eq.) and 0.058 g
 of B (0.22 mmol; 1 eq.) are placed in 10 ml of
 acetonitrile. 338 mg of 35% sodium hydroxide diluted in
 10 ml of water are then added, immediately followed by
 499 mg of CAN. The solution turns a grey-blue colour
 10 within a few minutes. After stirring for 4 hours,
 100 ml of water are added. The aqueous phase is
 extracted with ethyl acetate. The organic phase is
 removed. The aqueous phase is re-extracted with
 butanol. The butanol phase is then dried over sodium
 15 sulphate, filtered and then concentrated. The product
 is taken up in ethanol (2 ml) and then reprecipitated
 in diisopropyl ether. A black powder is obtained (C).

Mass (ES⁺): m/z: 438 (MH⁺)

20

By following the synthetic process described
 above, the compounds below may be obtained according to
 the indicated synthetic scheme:

62



Evaluation in the dyeing of keratin fibres

Each of the dyes of the preceding examples is mixed in the medium below to form a dye composition (0.5% by weight of dye). Keratin fibres are then added
5 to the composition thus obtained (composition/fibre ratio = 10/1). After 30 minutes, the hair is rinsed with water and then dried. A black coloration of the hair is thus obtained.

10 Dyeing medium

0.768% hydroxyethylcellulose
0.064% parabens
10% decyl glucoside
8% benzyl alcohol
15 12% propylene glycol
10% pH 7 buffer
water qs 100%